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Phase Space Wannier Functions in Electronic Structure Calculations

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ABSTRACT: We consider the applicability of "phase space Wannier functions" to electronic structure calculations. These generalized Wannier functions are analogous to localized plane waves and constitute a complete, orthonormal set which is exponentially localized both in position and momentum space. Their properties are described and an illustrative application to bound states in one dimension is presented. Criteria for choosing basis set size and lattice constant are discussed based on semi-classical, phase space considerations. Convergence of the ground state energy with respect to basis size is evaluated. Comparison with plane-waves basis sets indicates that the number of phase space Wannier functions needed for convergence can be significantly smaller in three dimensions.

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I. INTRODUCTION

This paper deals with a new set of generalized Wannier functions[1] (WF) which we argue has many advantages as a basis for large scale electronic structure calculations. The term Wannier functions refers to a complete and orthonormal set of *local* basis functions for representations of scalar wave functions. An example is the set of WF which span the same function space as the Bloch functions for a given energy band, or set of energy bands, in a crystal.[2] Though they are often useful as a theoretical tool, energy band WF have seldom been practical in quantitative electronic structure calculations. There are several reasons for this: One difficulty is the numerical complexity of their construction; they are not the solutions of any simple differential equation and often must be constructed from non-orthogonal trial functions. Second, the advantage of their mutual orthogonality is offset by the existence of long range oscillatory tails which are necessary to ensure their orthogonality. Band WF are, however, exponentially localized[2] provided there is a finite band-gap, and good localization is an essential requirement in quantitative calculations. One can define local Wannier functions which span the same function space as the plane waves in a given Brillouin zone, but such WF decay only algebraically and are of little practical use.

"Generic" basis functions, *i.e.,* functions with similar analytical structure, are particularly advantageous in large scale electronic structure calculations. Examples of generic functions are plane waves and and gaussians, which are often used in electronic structure calculations.[3] Evidently, the ease of computing Hamiltonian matrix elements with such analytical bases outweighs their disadvantages, namely, non-locality in the case of plane waves or non-orthogonality in the case of gaussians. Generic basis functions would appear to be especially desirable for vector or parallel computations. In contrast, an important disadvantage of energy band WF is that they are not generic; their form depends on a given atomic environment and hence, they must be recomputed in the course of self-consistent

calculations.

When the size of the basis becomes large, however, it becomes computationally advantageous to trade simplicity of matrix element construction in favor of a smaller, if more complicated basis. Sparseness of the Hamiltonian matrix is also a significant advantage. Yet another consideration is completeness. In the case of gaussians, it is not always clear whether the largest bases that can be implemented are sufficiently complete to cover the Hilbert space of interest. On the other hand, gaussian basis functions may be centered on arbitrarily positioned atoms, allow for spherical symmetry, and can represent well the cusps in atomic wavefunctions due to the divergence in the Coulomb potential. Mixed basis sets, *e.g.,* a combination of gaussians and plane waves,[4] have also been used. In general, such non-orthogonal bases can become overcomplete, as the finite basis is almost linearly dependent, and care must be taken to avoid numerical difficulties.

These considerations suggest that desirable basis functions for large scale electronic structure calculations should be orthogonal, complete, generic, local and possess useful analytic properties. To minimize basis set size, their locality should apply both to position and momentum space. A set of functions which has all of these desired properties are the generalized Wannier functions[1] $w_{l,n}(x)$ introduced by one of us. Here l and n are momentum and site labels, respectively. In this paper we discuss the potential applicability of these Wannier functions, hereafter referred to as "phase space Wannier functions" (PWF), to electronic structure calculations. Like plane waves, the PWF form a complete set and have simple matrix elements with respect to the kinetic energy operator $p^2 = -\nabla^2$, thereby simplifying the calculation of Hamiltonian matrix elements. Like gaussians, they are well localized in position space, and matrix elements with respect to simple functions, *e.g.,* 1, x, x^2, ... may be stored. Moreover, they are shown below to be localized exponentially in both position and momentum space. This leads to a sparse Hamiltonian matrix and an overall basis set size which can be significantly smaller than that with plane waves. These properties suggest

that the PWF functions have significant advantages in large scale electronic structure calculations, and we argue that they are a potential replacement or supplement to plane wave and gaussian basis sets. These considerations have been checked by carrying out a detailed one-dimensional, model calculation with the PWF with convergence checks and comparisons with other approaches. However, a full scale test of the basis, *e.g.,* with pseudopotentials and self-consistency remains to be done.

The paper is organized as follows: In section II the basic properties of the functions $w_{l,n}(x)$ are given, together with an algorithm for their construction and a demonstration of their exponential localization. Some generalizations are also discussed. In section III the utility of these Wannier functions is illustrated with a simple one-dimensional model. Criteria for choosing the basis set size and lattice constant are determined, and convergence of the ground state energy with respect to basis size is evaluated. Section IV contains a summary and conclusions.

II. PROPERTIES

In this section we summarize the properties of the phase space Wannier functions (PWF) introduced in Ref. 1. In addition some generalizations are introduced and their localization properties in position and momentum space are established.

A. Definitions

By construction the PWF $w_{l,n}(x)$ are uniform translations of real functions $w_l(x)$, localized about the sites of a regular lattice $x = na$ in position space

$$w_{l,n}(x) = w_l(x - 2\pi n). \tag{2.1}$$

Here a is an arbitrary lattice constant, which for convenience is set to 2π, l is a non-negative integer momentum index, as discussed below, and n is an integer site index; the functions $w_l(x)$ are of even(odd) parity for l even(odd). For other choices of a, normalized PWF are given by scaling the above functions:

$$w_{l,n}(x; a) = (2\pi/a)^{1/2}\, w_{l,n}(2\pi x/a). \tag{2.2}$$

The functions $w_{l,n}$ are orthogonal and normalized such that their inner product is a delta function:

$$\langle w_{l,n} | w_{l',n'} \rangle = \delta_{ll'}\delta_{nn'}. \tag{2.3}$$

The set of $w_{l,n}(x)$ constructed in Ref. 1 are illustrated in Fig. 1(a) for $0 \leq l \leq 2$.

In momentum space, Eq. (2.1) becomes

$$\tilde{w}_{l,n}(p) = e^{-ip2\pi n}\tilde{w}_l(p). \tag{2.4}$$

where $\tilde{w}_{l,n}(p)$ is the Fourier transform of $w_{l,n}(x)$. The function $\tilde{w}_l(p)$ is peaked bimodally in momentum space, as illustrated in Fig. 1(b). More precisely, $\tilde{w}_l(p)$ is a real(pure imaginary)

function of even(odd) parity for even(odd) l, and is peaked near $p = \pm\frac{1}{4}(2l+1)$ (except for $l = 0$ which is peaked only at the origin). Each function $\tilde{w}_l(p)$ roughly covers the disjoint intervals $[\frac{1}{2}l, \frac{1}{2}(l+1)]$ and $[-\frac{1}{2}(l+1), -\frac{1}{2}l]$ in p, decaying exponentially rapidly into neighboring intervals. Thus one may imagine that phase space $[-\infty < x < \infty, -\infty < p < \infty]$ may be spanned in terms of "fuzzy" rectangular blocks each represented by a function $w_{l,n}$ either in position or momentum space (Fig. 2), whence our description "phase space Wannier functions." This localization property permits the basis to be tailored at a given site n simply by increasing the number of momentum states $l_{max}(n)$ that are used without altering the form of the functions, changing the lattice constant a, or warping space.

Several additional properties are needed to define the PWF uniquely. For example the functions of Ref. 1 are defined to have simple matrix elements with respect to the kinetic energy operator $p^2 = -d^2/dx^2$,

$$\langle w_{l,n}|p^2|w_{l',n'}\rangle = \begin{cases} \alpha_l\ (\delta_{n,n'-1} - \delta_{n,n'+1}), & l = l'+1; \\ \beta_{l,n-n'}, & l = l'; \\ \alpha_{l'}\ (\delta_{n,n'+1} - \delta_{n,n'-1}), & l = l'-1; \end{cases} \tag{2.5}$$

where[1] $\alpha_l = l/(4\pi)$ and $\beta_{l,n}$ decays exponentially rapidly with $|n|$. The $\beta_{l,n}$ are computed numerically in momentum space using Eq. (2.5). Choices of dispersion other than p^2 will be discussed below.

The three-dimensional generalizations of these functions are, as in the case of plane waves, Cartesian products, which are labelled by vector indices, $\vec{l}$ and $\vec{n}$,

$$w_{\vec{l}\vec{n}}(\vec{r}) = w_{n_x,l_x}(x) w_{n_y,l_y}(y) w_{n_z,l_z}(z). \tag{2.6}$$

The product form of Eq. (2.6) can considerably simplify the computation of matrix elements; for example, matrix elements of separable operators such as $\exp(-\lambda r^2)$ factor into one dimensional products. Thus matrix elements of the Coulomb potential can be computed as a single one-dimensional integral of a product of three one-dimensional matrix elements by use of the identity $(1/r) = (2\pi^{-1/2}) \int_0^\infty d\kappa \exp(-\kappa^2 r^2)$.

The functions $w_{l,n}(x)$ have a number of other useful analytical properties. For example the coefficients $c_{l,n}$ in the Wannier function expansion,

$$f(x) = \sum_{l,n} c_{l,n} w_{l,n}(x), \tag{2.7}$$

of a function $f(x)$ with a Taylor expansion about $x = na$ are related to the Taylor series coefficients of $f(x)$ at na as follows:

$$\begin{aligned} c_{0,n} =& a^{\frac{1}{2}} \left(f(na) + \tfrac{1}{2} f''(an) (\frac{a}{2\pi})^2 + O(f^{(iv)}(na) a^4) \right) \\ c_{1,n} =& a^{\frac{1}{2}} \left(-f'(an) (\frac{a}{2\pi}) + O(f'''(an) a^3) \right) \\ c_{2,n} =& a^{\frac{1}{2}} \left(2f''(an) (\frac{a}{2\pi})^2 + O(f^{(iv)} a^4) \right). \end{aligned} \tag{2.8}$$

Equation (2.8) follows from the relation between the moments of $w_{l,n}(x)$ and the derivatives of $\tilde{w}_{l,n}(p)$ at $p = 0$, as discussed in Appendix A.

As a consequence, the expansion of the constant function requires only the $l = 0$ PWF (at all sites); the expansion of a linear function requires only the $l = 0$, and 1 functions (at all sites); and so on. This result holds *locally* as well: in the neighborhood of a site $x = na$ the first two PWF's ($l = 0, 1$) adequately represent an arbitrary function as long as it does not vary rapidly on the scale of a. For sufficiently narrow cells, these functions therefore serve as a complete set of "shape functions," as in the finite element method of Ref. 5. While the shape functions of the finite element method can be more compact, their finite range leads to poor convergence in momentum space; also, these shape functions are polynomial complete only to some low order.

B. Algorithm for Construction of $w_{l,n}$

An algorithm together with a *Gibbs description* of a computer code for constructing PWF $w_{l,n}$ with the above properties has been given in Ref. 1. In this Section we present an

alternative procedure which has the following advantages: The Wannier functions generated can be shown to form a complete and orthogonal basis, and the new procedure can be generalized to make use of dispersions other than p^2. Lastly, a recursion relation for the PWF is discussed.

To prove completeness, and orthogonality of the PWF basis, we show that the PWF's are the eigenfunctions of a Hermitian matrix H representing the operator $p^2 = -d^2/dx^2$. The diagonal matrix elements of H, which are determined from the $\beta_{l,n}$, are not known beforehand, but are computed by an iterative method.

The site-translation property of Wannier functions allows one to work in a reciprocal space description in which $p = m + q$ with m an integer, and q in the first Brillouin zone. In this picture the orthogonality relation, Eq. (2.3) becomes

$$\sum_n \langle w_{l,0}|w_{l',n}\rangle e^{2\pi iqn} = \sum_{m=-\infty}^{+\infty} \tilde{w}_l^*(m+q)\tilde{w}_{l'}(m+q) = \delta_{ll'}. \tag{2.9}$$

Similarly, defining $H_{l,l'}(q) = \Sigma_n \langle w_{l,0}|p^2|w_{l',n}\rangle e^{2\pi iqn}$, the p^2 matrix elements, Eq. (2.5), become

$$H_{l,l'}(q) \equiv \sum_{m=-\infty}^{+\infty} \tilde{w}_l^*(m+q)\tilde{w}_{l'}(m+q)\,(m+q)^2 = \begin{cases} 2i\alpha_l \sin 2\pi q, & l = l'+1; \\ \beta_l(q), & l = l'; \\ -2i\alpha_{l'} \sin 2\pi q, & l = l'-1; \end{cases} \tag{2.10}$$

with $\alpha_l = l/(4\pi)$, and $\beta_l(q) \equiv \Sigma_n \beta_{l,n} e^{2\pi inq}$.

For each q, the tridiagonal matrix $H_{l,l'}(q)$ defines an eigenvalue problem for which the eigenvalues are known explicitly, and the eigenfunctions are the desired PWF.

$$\sum_{l'=0}^{\infty} H_{l,l'}(q)\tilde{w}_{l'}(m+q) = (m+q)^2 \tilde{w}_l(m+q). \tag{2.11}$$

The diagonal elements of $H_{l,l'}(q)$ are computed numerically as follows: First, the range of l is made finite by limiting it to $\{0, \cdots, L\}$ with L even. The set of eigenvalues is also truncated to $\{(-\frac{1}{2}L+q)^2, (-\frac{1}{2}L+1+q)^2, \cdots, (\frac{1}{2}L+q)^2\}$ to reflect the truncated momentum space. The truncation introduces significant error in quantities near the upper end of momentum

space; for example, the values of $\beta_L(q)$, $\tilde{w}_L(m+q)$, and $\tilde{w}_0(\frac{1}{2}L+q)$ computed in this approximation differ significantly from their true values. On the other hand, the effects of truncation diminish rapidly as one moves away from the upper end, and accurate $\beta_l(q)$ can be computed for l small compared to L.

We evaluate the characteristic equation for each of the $L+1$ eigenvalues to obtain a set of equations determining the $L+1$ unknowns $\beta_l(q)$,

$$\det|H_{l,l'}(q) - (m+q)^2\delta_{l,l'}| = 0, \quad \text{for } m = \{-\tfrac{1}{2}L, \cdots, \tfrac{1}{2}L\}. \tag{2.12}$$

These equations may be solved by a fixed-point iterative scheme as each $\beta_l(q)$ may be readily expressed in terms of the others because the determinant is linear in each $\beta_l(q)$.[6] The expected bimodality of the $\tilde{w}_l(p)$ suggests that the starting values for the $\beta_l(q)$ be chosen to be near $(\frac{1}{2}l+q)^2$ for l even, and $(-\frac{1}{2}(l+1)+q)^2$ for l odd. Once the $\beta_l(q)$ are known, a quick diagonalization yields the $\tilde{w}(m+q)$.

Note that the method of Ref. 1 was to solve for the $\tilde{w}_l(p)$ without computing the $\beta_l(q)$ first. This is more efficient and is the preferred method for generating the PWF basis; however, the present prescription can also be generalized to dispersions other than p^2 as discussed in Section II C, below.

Recursion relations between the functions $\tilde{w}_l(p)$ are also useful. From the matrix elements in Eq. (2.5) one has

$$\alpha_{l+1}\,\tilde{w}_{l+1}(p) = \alpha_l\,\tilde{w}_{l-1}(p) + \frac{(p^2-\beta_l(p))}{2i\sin 2\pi p}\,\tilde{w}_l(p), \qquad (l \geq 0,\ \alpha_0 = 0), \tag{2.13}$$

Thus, given the function $\tilde{w}_0(p)$, the remaining functions and the $\beta_l(p)$ can be determined in principle by recursion. Note that the functions $\tilde{w}_l(p)$ have zeros at the half integers (at which the denominator $2i\sin 2\pi p$ vanishes) with the exception of $p = \pm\frac{1}{2}l$, and $p = \pm\frac{1}{2}(l+1)$ (at which the numerator $p^2-\beta_l(p)$ also vanishes). Tables of the functions $\tilde{w}_l(p)$ are available from the authors.

C. Generalization to Arbitrary Dispersion

An advantage of the construction algorithm outlined in Section II B is that the generalization to other dispersions $H = \epsilon(p)$ is easily carried out. We consider only dispersions that do not have the periodicity of the reciprocal lattice and are even functions of p. Under these restrictions the generalized WF can be chosen to have definite parity and cover the phase space in the same manner as before.

Matrix elements of the dispersion are again required to have a tridiagonal form: Eqs. (2.10) and (2.11) are replaced by

$$H_{l,l'}(q) \equiv \sum_{m=-\infty}^{+\infty} \tilde{w}_l^*(m+q)\tilde{w}_{l'}(m+q)\,\epsilon(m+q) = \begin{cases} 2i\alpha_l \sin 2\pi q, & l = l'+1; \\ \beta_l(q), & l = l'; \\ -2i\alpha_{l'} \sin 2\pi q, & l = l'-1; \end{cases} \tag{2.14}$$

with $\beta_l(q) \equiv \Sigma_n \beta_{l,n} e^{2\pi i n q}$ and

$$\sum_{l'=0}^{\infty} H_{l,l'} w_{l'}(m+q) = \epsilon(m+q) w_l(m+q). \tag{2.15}$$

By an analysis similar to that of Ref. 1 we find[7] that the coefficients α_l are given by $\epsilon'(\frac{1}{2}l)/4\pi$, where $\epsilon'(p) = d\epsilon(p)/dp$. The remaining steps of the construction procedure are carried out as in the previous section. The iteration is started with the $\beta_l(q)$ chosen to be near $\epsilon(\frac{1}{2}l + q)$ for l even, and $\epsilon(-\frac{1}{2}(l+1) + q)$ for l odd. The effect of dispersion on the PWF is illustrated in Fig. 3, where functions for the dispersions $\epsilon(p) = p^2$ and $\epsilon(p) = p^4$ are compared.

D. Exponential Localization

The Wannier functions $w_{l,n}$ of Ref. 1 appear to be localized exponentially in position space and their fourier transforms in momentum space. This is surprising in view of a theorem proved independently by Balian and by Low,[8] which shows that it is impossible to construct Wannier functions which are exponentially localized about the sites of a regular

lattice in phase space with cell area 2π. In this section we discuss how this theorem can be evaded to construct functions which do possess exponential localization.

The non-existence theorem of Ref. 8 applies specifically to functions which are uniform translations in phase space of a singly peaked function $f(p)$, as in the functions of von Neumann,[9]

$$g_{l,n}(p) = f(p-l)e^{-i2\pi pn}, \tag{2.16}$$

for integers l, n. As a consequence expansions in "coherent states," where $f(p)$ is a gaussian, converge very slowly (*i.e.,* algebraically), so their usefulness in quantitative calculations is limited. By contrast, the PWF are bimodal in phase space. They are composed of functions peaked about $p = \pm\frac{1}{4}(2l+1)$, as in

$$g_{l,n}(p) = \left[f(p-\tfrac{1}{4}(2l+1)) + (-1)^l f(-p-\tfrac{1}{4}(2l+1))\right] e^{-i2\pi pn}, \tag{2.17}$$

for integers $l \geq 0$ and n. This bimodal form is sufficient to render the theorem in Ref. 8 inapplicable. Strictly speaking, the bimodal form of $g_{l,n}(p)$ implies that the rms width of such functions in momentum space is $O(l)$ for large l; but the two peaks $f(p)$ in Eq. (2.17) are each well localized about $|p| = \frac{1}{4}(2l+1)$.

To see how bimodality of $g_{l,n}$ leads to exponential localization, we consider the problem of generating a complete set of orthonormal, Wannier functions $w_{l,n}$ starting from *trial functions* of the form of Eq. (2.17), where $f(p)$ is a normalizable, even function assumed to be well localized about the origin. The functions $w_{l,n}$ are constructed [2] by a symmetric orthogonalization of the functions $g_{l,n}$, using the inverse square root of the overlap matrix $S_{ln,l'n'} = \langle g_{l,n}|g_{l',n'}\rangle$:

$$w_{l,n} = \sum_{l',n'} (S^{-1/2})_{ln,l'n'}\, g_{l',n'}. \tag{2.18}$$

The matrix $S^{-1/2}$ can be calculated by going to a diagonal representation in terms of the

solutions to the eigenvalue problem,

$$\sum_{l',n'} S_{ln,l'n'}\, c_{l',n'} = \lambda c_{l,n}. \tag{2.19}$$

This construction is carried out in Appendix B where it is shown that $(S^{-1/2})_{ln,l'n'}$ decays exponentially both in $|n - n'|$ and in $|l - l'|$ for large l. This result implies exponential localization[10] with the same decay constants for the Wannier functions, $w_{l,n}$ defined by Eq. (2.18), for sufficiently localized trial functions $f(p)$ (*e.g.,* gaussians). Moreover, the translational invariance $(S^{-1/2})_{ln,l'n'}$ in l for large l implies that the Wannier functions in momentum space will be nearly identical for large l, a form which is already evident from Fig. 1(b).

III. APPLICATION TO QUANTUM MECHANICS IN ONE-DIMENSION

A. Schrodinger Equation in the PWF Basis

As an illustration of their properties and the application of the PWF we use them as a basis for solving the one-dimensional Schrodinger equation

$$H\psi = \left[-\frac{d^2}{dx^2} + V(x)\right]\psi = E\psi. \tag{3.1}$$

We take $V(x)$ to be an attractive single-well potential of the form

$$V(x) = -\lambda\ \mathrm{sech}^2(x), \tag{3.2}$$

with $\lambda = 35/4$ (Fig. 4). For this choice, the bound state solutions $\psi(x)$ are known analytically, so that precise comparisons are possible: there are three bound states of which the lowest is at $E_0 = -25/4$, and $\psi_0 = (8/3\pi)^{1/2}\mathrm{sech}^{5/2}(x)$.

In the PWF basis, $\psi(x) = \Sigma_{ln}\, c_{ln}\, w_{ln}(x)$, and the Schrodinger equation (3.1) is equivalent to the matrix eigenvalue problem,

$$\sum_{l'n'} H_{ln,l'n'}\, c_{l'n'} = E\, c_{ln}. \tag{3.3}$$

It is convenient to compute the kinetic energy part of H in momentum space using Eq. (2.5) and the potential energy part in position space, so that

$$H_{ln,l'n'} = \tfrac{1}{2}\langle w_{ln}|p^2|w_{l'n'}\rangle + \langle w_{ln}|V(x)|w_{l'n'}\rangle. \tag{3.4}$$

The sum over n' in Eq. (3.3) is restricted to box of length L so that $-\frac{1}{2}L \le x = na \le \frac{1}{2}L$, for a given choice of L and lattice constant a, while that over l' is restricted to $l' \le l_{max}(n')$. The exact coefficients $c_{l,n}$ can be obtained conveniently in momentum space,

$$c_{l,n} = \int dp\, w^*_{l,n}(p)\psi_0(p), \tag{3.5}$$

where $\psi_0(p) = (8/3\pi)(2/3\pi)^{1/2}|\Gamma(\frac{5}{4} + \frac{1}{2}ip)|$. These coefficients are given in Table 1 for lattice constants $a = 0.5, 1.5$, and 3.5, and a fixed overall length $L = 10.5$, a value chosen to be a few times the width of the potential well $V(x)$. Choosing, for example, 0.01 as a cutoff for the phase-space cell occupations $|c_{l,n}|^2$, the representation of the ground state wave function requires 5 PWF, *i.e.,* $(l = 0; n = 0, \pm 1, \pm 2)$, for lattice constant $a = 0.5$; 3 PWF, *i.e.,* $(l = 0; n = 0, \pm 1)$, for $a = 1.5$; and just 2 PWF, $(l = 0, 2, n = 0)$, for a=3.5. For comparison, a plane wave basis to the same 1% accuracy requires 9 plane waves, $k = 2\pi m/L$ with $-4 \leq m \leq 4$ (see Table 2). With the cutoff set at 0.003, the corresponding numbers are 7 Wannier functions for $a = 0.5$, 5 for $a = 1.5$, 6 for $a = 3.5$, and 11 plane waves. Note that the example we have chosen is centered at $x = 0$, so some coefficients vanish automatically; similarly, if symmetrized plane waves were used, only 5 (or 6 for a cutoff of 0.003) even functions would be needed. However, in practice one cannot assume symmetry. Without symmetry, the $n = 0, l = 1$ amplitudes need not vanish, increasing the counts for the Wannier functions by one for all three values of a; similarly one needs all plane waves. Note also that the number of plane waves needed depends on the length of the system L, while the number of Wannier functions is determined locally and is independent of L. In the present example, the number of plane waves can be reduced by cutting down L, but this restricts the location of the orbital.

B. Phase Space Criteria for Basis Set Size

We now discuss the dependence of the coefficients $c_{l,n}$ on l and n from phase-space considerations. To the extent that a semi-classical description is valid, these coefficients should be small for all phase space cells which do not overlap the classical trajectory. This indeed appears to be the case and suggests a criterion for adopting a given lattice constant and basis set size. One choice of the lattice constant a is that value for which the "coverage"

$\sum_{occ} |c_{l,n}|^2$ is optimal, *i.e.,* the value for which the minimum number of phase space cells overlap the classical region of occupied states. From Table 1 the coverages at a cutoff of 0.01 in $|c_{l,n}|^2$ are 0.978, 0.985 and 0.975 for lattice constants $a = 0.5$, 1.5, and 3.5, respectively. For a cutoff of 0.003, the corresponding figures are 0.990, 0.999 and 0.997. For both cutoff choices, the value $a = 1.5$ maximizes the coverage with a minimum number of functions and is therefore optimal for the values being considered. Inspection of Fig. 5 indicates that this lattice constant corresponds roughly to the size of the phase space orbit. Were the lattice constant chosen to differ greatly from this value, the phase space cells would not "tile" the orbit efficiently, and more PWF's would be needed to achieve comparable coverage of the ground state wavefunction.

For comparison, a plane wave expansion spans phase space with elongated cells of width $\Delta x = L$ and height $\Delta p = 2\pi/L$, and therefore requires $2p_{max}L/2\pi$ states, for an equivalent description. The value of p_{max} is related to the depth of a potential well. For example, in the case of a point charge Ze, $\psi(x) \sim \exp(-Zx/a_o)$ and $p_{max} \sim Z/a_o$, where a_o is the Bohr radius. The use of pseudopotentials, therefore, can considerably reduce the size of basis required for a given calculation, either in a plane-wave or a PWF basis. Moreover, one expects from general phase space volume considerations (*i.e.,* from the uncertainty principle) that the number of Wannier functions needed will be of order $2\int dx\, p(x)/2\pi\hbar$ which is just the area of phase space within the classical orbit at energy E, in units of $2\pi\hbar$. The Wannier functions are therefore expected to be more efficient than the plane waves by a factor roughly equal to the ratio of these phase-space areas (phase-space volumes in three dimensions). It is also of interest to examine the convergence of the "coverage" *vs.* total basis size. For smooth potentials, the convergence of the coverage with respect to l at a given n appears to be exponentially rapid, which is what one expects based on WKB arguments. For the one-dimensional example discussed above, it is observed that the number of plane waves required to give an accuracy of 1% (or 0.3%) in the coverage is, ignoring symmetry, about

9/6 (or 11/6) times that for the Wannier functions; in three dimensions the corresponding factor would be cubed, *i.e.,* with the plane wave basis larger by a factor of 3 to 6, depending on the choice of cutoff. Thus because it can be adjusted locally, the PWF basis can be significantly smaller than a plane wave basis.

C. Convergence of Ground State Energy

Finally, we have computed the coefficients $c_{l,n}$ and the eigenvalue E_0 for the lowest state by straightforward diagonalization of the Hamiltonian matrix in Eq. (3.3) for several different basis set sizes. The results are shown in Table 3. Note that convergence of the ground state energy and the convergence of the coverage are comparable since both vary quadratically with wavefunction error. For example, for the case $a = 1.5$ with 5 basis functions the difference from unity of the coverage, *i.e.,* $1 - \Sigma|c_{l,n}|^2$, is 0.0027, and the relative error in the ground state energy, $\Delta E_0/E_0$, is 0.0008. For $a = 3.5$ with 6 basis functions, the corresponding numbers are 0.0046 and 0.0102, respectively. This also indicates the importance of total coverage as a gauge of convergence of a given basis set.

IV. CONCLUSIONS

We have suggested that phase space Wannier functions may be an attractive basis for large scale electronic structure calculations, as they constitute an orthonormal, complete, local and generic basis set. Their localization in position and momentum space permits the basis set to be optimized locally, and they have many convenient properties, *e.g.,* simple short-range matrix elements of the kinetic energy operator. On the other hand, we have not constructed an analytical representation of these functions; at present, they are tabulated numerically, and typically 100 points are needed to represent their fine structure. Detailed properties of these functions and some generalizations have been given, together with an algorithm for their construction and proof of their exponential localization properties.

An illustrative application to the Schrodinger equation in one-dimension has also been given. The results of our one-dimensional example suggest criteria for choosing the basis set size and lattice constant a based on semi-classical, phase space considerations. Compared with a plane wave basis set, the phase space Wannier functions permit a significant reduction in basis set size, since the basis size can be adjusted locally. Even a small reduction is significant in three dimensions, since the number of operations required in a straightforward matrix diagonalization varies as the cube of the basis size.

The next step would be to carry out a three-dimensional electronic structure calculation using these functions, i.e., a calculation analogous to a comparable plane-wave, pseudopotential calculation. Important developments needed for self-consistent calculations are a) a good representation of pseudopotential matrix elements, and b) an efficient scheme for solving Poisson's equation in the PWF basis.

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APPENDIX A

Taylor and Wannier Function Expansion Coefficients

In this appendix we discuss the relation between the Wannier function expansion coefficients $c_{l,n}$ of a function $f(x)$,

$$f(x) = \sum_{l,n} c_{l,n}\, w_{l,n}(x;a), \qquad c_{l,n} = \int dx\, w_{l,n}(x;a)\, f(x), \tag{A1}$$

and the Taylor series expansion coefficients of $f(x)$ about the point $x = na$, *i.e.,*

$$f(x) = \sum_{j} \frac{f^{(j)}(na)}{j!}(x - na)^j. \tag{A2}$$

Using equations (A1), (A2) and (2.2), two expressions for the expansion coefficients are readily obtained.

$$\begin{aligned} c_{l,n} &= (a/2\pi)^{\frac{1}{2}} \sum_{j} \frac{f^{(j)}(na)}{j!}(a/2\pi)^j \int dx\, x^j\, w_l(x) \\ &= (a/2\pi)^{\frac{1}{2}} \sum_{j} \frac{f^{(j)}(na)}{j!}(a/2\pi)^j\, \mu_{l,j} \\ &= a^{\frac{1}{2}} \sum_{j} \frac{f^{(j)}(na)}{j!}(ia/2\pi)^j\, \tilde{w}_l^{(j)}(0) \end{aligned} \tag{A3}$$

where $\mu_{l,j}$ is j^{th} moment of $w_l(x)$, and $\tilde{w}_l^{(j)}(p)$ is the j^{th} derivative of $\tilde{w}_l(p)$. This last equation follows from the equality between the moments and the derivatives of $\tilde{w}_l(p)$ evaluated at the origin.

$$\mu_{l,j} = (2\pi)^{\frac{1}{2}}\, i^j \tilde{w}_l^{(j)}(0). \tag{A4}$$

Now: the sum in Eq. (A3) simplifies considerably since (a) many of the moments vanish by symmetry arguments, and (b) many more vanish by the structure of the $\tilde{w}_l(p)$ at the

origin. From the recursion relation Eq. (2.13) one can determine the location as well as the order of the zeros of $\tilde{w}_l(p)$. In particular, at the origin the following derivatives vanish,

$$\tilde{w}_l^{(j)}(0) = 0 \quad \text{for } j < l. \tag{A5}$$

Further, several of the non-vanishing derivatives can be deduced from the recursion and the orthogonality equations: $\tilde{w}_0(0) = 1$, $\tilde{w}_0''(0) = -1$, $\tilde{w}_1'(0) = i$, $\tilde{w}_2''(0) = -4$; the remaining derivatives, if needed, can be calculated numerically. Using Eq. (A3) and known values of the derivatives, we obtain the results given in Eq.(2.8).

APPENDIX B

Exponential Decay of Phase Space Wannier Functions

In this section we construct the inverse square root $(S^{-1/2})_{ln,l'n'}$ of the overlap matrix $S_{ln,l'n'} = \langle g_{l,n}|g_{l',n'}\rangle$ for a set of trial Wannier functions $g_{l,n}$ given by Eq. (2.17). The computation is most conveniently carried out in a diagonal representation, *i.e.,* in terms of the eigenstates $c_{l,n}$ of the matrix $S_{ln,l'n'}$:

$$\sum_{l',n'} S_{ln,l'n'} c_{l',n'} = \lambda c_{l,n}. \tag{B1}$$

This calculation is carried out in several steps as follows. First by translational invariance in position space, we may take $c_{l,n}$ to be of Bloch form, $c_{l,n} = c_l(k)\exp(ikn)$ so that Eq. (B1) reduces to a one-dimensional eigenvalue problem, $\Sigma_{l'} S_{l,l'}(k) c_{l'}(k) = \lambda_k c_l(k)$, where $S_{l,l'}(k) = \Sigma_n \exp(2\pi ikn) S_{l0,l'n}$. Second, note that by construction the form of the matrix $S_{l,l'}(k)$ depends on whether l and l' are even or odd. Thus we define $l \equiv 2\mu + \sigma$, $(\sigma = 0, 1)$. We find below that for large l, l' the matrix $S_{l,l'}(k)$ becomes translationally invariant in μ. The eigenvalue problem is thus analogous to a tight-binding problem on a semi-infinite chain with two basis states $(\sigma = 0, 1)$ per unit cell. The limiting form of $S_{l,l'}(k)$ is seen to be

$$S_{l,l'}(k) \to S_{\sigma\sigma'}(k, \mu - \mu') = \left[\tilde{S}_{\sigma\sigma'}(k, \mu - \mu') + (-1)^{\sigma+\sigma'} \tilde{S}_{\sigma\sigma'}(-k, \mu - \mu')\right], \tag{B2}$$

where nontranslationally invariant terms which vary as $\tilde{S}_{\sigma,\sigma'}(k, \mu + \mu')$ have been neglected; those terms are negligible for sufficiently localized functions f. In terms of the functions $f(p)$ in Eq. (2.17) the quantity in Eq. (B2) is

$$\tilde{S}_{\sigma,\sigma'}(k, \mu) = \sum_m f(k + m - \tfrac{1}{4}(\sigma + 1))\, f(k + m + \mu - \tfrac{1}{4}(\sigma + 1)). \tag{B3}$$

Next, the eigenvalues of Eq. (B1) can be obtained from the large l limit where, by translational invariance in μ, $c_l(k) \to \exp(\pm i 2\pi q\mu) c_\sigma(k, q)$. Then one obtains the 2×2 eigenvalue

problem,

$$S_{\sigma,\sigma'}(k,q)c'_{\sigma}(k,q) = \lambda_{k,q}c_{\sigma}(k,q), \tag{B4}$$

where

$$S_{\sigma,\sigma'}(k,q) = \sum_{\mu} S_{\sigma\sigma'}(k,\mu)e^{iq\mu} = \tilde{S}_{\sigma,\sigma'}(k,q) + (-1)^{\sigma+\sigma'}\tilde{S}_{\sigma,\sigma'}(-k,q). \tag{B5}$$

It is easily verified that the functions $\tilde{S}_{\sigma,\sigma'}$ factor as $\tilde{S}_{\sigma,\sigma'}(k,q) = \theta^*_{\sigma}(k,q)\theta_{\sigma'}(k,q)$, where

$$\theta_{\sigma}(k,q) = \sum_{m} e^{i2\pi qm} f(k+m-\tfrac{1}{4}(2\sigma+1)). \tag{B6}$$

The functions in Eq. (B6) are analogous to those discussed by Balian and by Low.[8] They show that $\theta_{\sigma}(k,q)$ must have at least one real zero in the Brillouin zone $[0 \le k \le 1, 0 \le q \le 1]$. This property is sufficient to rule out exponential decay for Wannier functions constructed from the singly-peaked trial functions of Eq. (2.16). For the functions $\theta_{\sigma}(k,q)$ one can also establish the identity $\theta_1(k,q) = \exp(i2\pi q)\theta^*_0(-k,q)$, from which it follows that the 2×2 matrix $S_{\sigma,\sigma'}(k,q)$ is diagonal, with diagonal elements given by $|\theta_0(k,q)|^2 + |\theta_1(k,q)|^2$. Hence, barring the unlikely possibility of common zeroes both in θ_0 and θ_1, the eigenvalues are positive definite for real k,q. For gaussian trial functions $f(p)$, for example, there is only a single zero of $\theta_0(k,q)$ at $q=\frac{1}{2}$ and $k=\frac{3}{4}$.

Finally, the inverse square root matrix is obtained by quadrature, and we obtain

$$(S^{-1/2})_{ln,l'n'} = \iint_{BZ} dk\, dq \sum_{\alpha=0,1} \frac{c^{\alpha}_l(k,q)c^{\alpha}_{l'}(k,q)}{[|\theta_0(k,q)|^2 + |\theta_1(k,q)|^2]^{1/2}} e^{i2\pi k(n-n')}, \tag{B7}$$

where $c_l(k,q) = A_l(k,q)\cos(q\mu + \delta_l(k,q))$ are the exact eigenstates, $\delta_l(k,q)$ being a phase shift which is l dependent for small l. Since the integrand has no zero for real k,q in the Brillouin zone, $(S^{-1/2})_{ln,l'n'}$ will decay exponentially in $|n-n'|$ and in $|l-l'|$ for large l, at rates determined by the nearest zeroes of $\lambda(k,q)$ in complex k,q space. Applying this result to Eq. (2.18), one sees that the Wannier functions $w_{l,n}$ have the same decay rates;[10] *i.e.,* there is decay constant $\bar{h}_n$ such that $\exp(hn)w_{l,n} \to 0, n\to\infty, h \le \bar{h}_n$, and similarly for decay with respect to l. In Ref. 1 these decay constants are found empirically to be $\bar{h}_n = 2.9$ and $\bar{h}_l = 0.46$, respectively.

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6. We can expand the determinant in powers of one of the $\beta_l(q)$: Setting $D[\beta_l(q)] = \det|H_{l,l'}(q) - (m+q)^2\delta_{l,l'}|$, one has $0 = D[\beta_l(q) + \Delta\beta_l(q)] = D[\beta_l(q)] + \Delta\beta_l(q)(\partial D[\beta_l(q)]/\partial\beta_l(q)) = D[\beta_l(q)](1 + \Delta\beta_l(q)G_{l,l}(q))$, where $G_{l,l'}(q)$ is the inverse of $H_{l,l'}(q) - (m+q)^2\delta_{l,l'}$. Solving for $\Delta\beta_l(q)$, we obtain $\Delta\beta_l(q) = -1/G_{l,l}(q)$. The diagonal elements of the inverse of a tridiagonal matrix are rapidly computable.

7. The analyticity of $\tilde{w}_l(p)$ as q approaches zero determines α_l: $\alpha_l = (\epsilon(q + \frac{1}{2}l) - \epsilon(q - \frac{1}{2}l))/[4\sin 2\pi q]$. Evaluating this expression using l'Hospital's rule fixes α_l to be $\epsilon'(\frac{1}{2}l)/4\pi$.

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FIGURE CAPTIONS

Fig. 1. Phase space Wannier functions w_l for the dispersion relation p^2 with lattice constant $a = 2\pi$ (a) in position space: $l = 0$, solid line; $l = 1$, dotted line; and $l = 2$, solid-dashed line; and (b) in momentum space, plotted with respect to the central momentum $(2l+1)/4$. For odd l, the imaginary part is plotted. Note that the functions are indistinguishable for $l \geq 2$.

Fig. 2. Schematic plot of phase space cells (disjoint for $l > 0$) corresponding to peaks in $w_{l,n}$ for (a) even l and (b) odd l. Also shown at is the approximate shape of $w_l(p)$ in momentum space.

Fig. 3. Effect of dispersion relation $\epsilon(p)$ on the PWF; shown are functions $w_l(p)$ in momentum space for dispersion relation p^2 (solid line) and p^4 (dashed line): $l = 0$ (upper curves) and the imaginary part of $W_l(p)$ for $l = 1$ (lower curves), all with lattice constant $a = 2\pi$.

Fig. 4. Potential $V(x) = -\lambda \operatorname{sech}^2(x)$ with $\lambda = 35/4$. Horizontal lines correspond to the three bound-state energy levels.

Fig. 5. Classical phase space orbits $p(x) = \sqrt{E_i - V(x)}$ of bound states of the potential $V(x) = -\lambda \operatorname{sech}^2(x)$ with $\lambda = 35/4$. Superposed are phase space cells for different choices of lattice constants: a) $a = 0.5$, b) $a = 1.5$, and c) $a = 3.5$. Tables of coefficients for these choices of a are given in Table 1.

TABLE CAPTIONS

Table 1. Contribution to the ground state wave function $|c_{l,n}|^2$ from the phase space cell l, n, for different choices of lattice constant: a) $a = 0.5$; b) $a = 1.5$; and c) $a = 3.5$.

Table 2. Contribution to the ground state wave function $|c_k|^2$ for a plane wave expansion in the interval $-L/2 \leq x \leq L/2$, with $L = 10.5$ and $k = 2\pi m/L$, for $m = 0, \pm 1, \pm 2, \cdots \pm 6$.

Table 3. Ground state energy E_0 for various basis set sizes $\{l, n\}$.

Table 1.

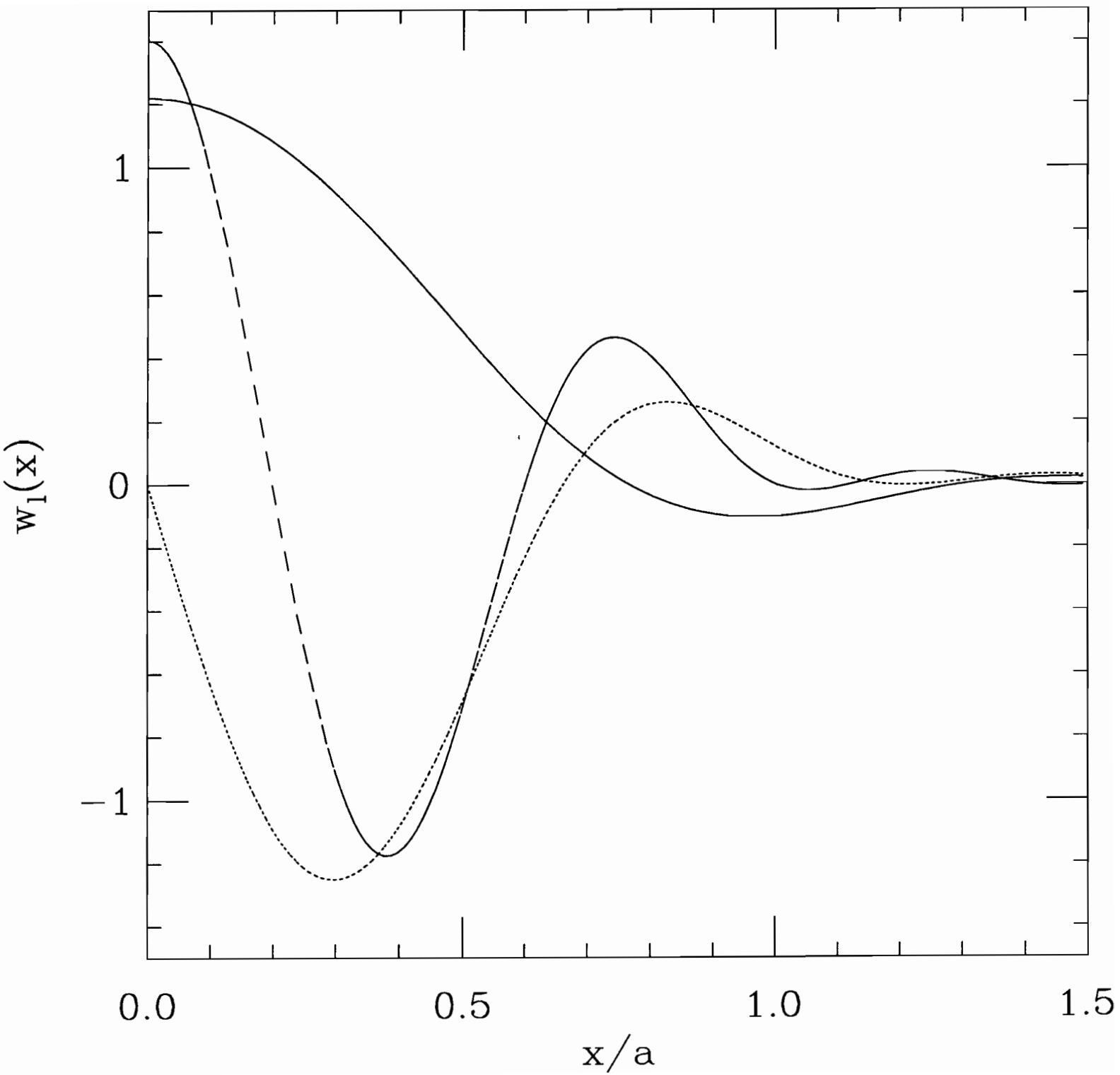
	$\|c_{l,n}\|^2$				
	$l \setminus n$	0	1	2	3
a = 0.5	0	0.41400	0.23226	0.04984	6×10^{-3}
	1	0.00000	3×10^{-3}	1×10^{-3}	2×10^{-4}
	2	2×10^{-4}	3×10^{-5}	2×10^{-5}	2×10^{-5}
a = 1.5	0	0.92235	0.03112	1×10^{-6}	5×10^{-7}
	1	0.00000	0.00731	4×10^{-5}	1×10^{-6}
	2	1×10^{-4}	1×10^{-6}	1×10^{-6}	1×10^{-6}
a = 3.5	0	0.84512	7×10^{-4}	1×10^{-5}	3×10^{-8}
	1	0.00000	5×10^{-3}	1×10^{-5}	2×10^{-8}
	2	0.12984	6×10^{-3}	3×10^{-5}	7×10^{-8}

Table 2.

k	$\|c_k\|^2$
0.0000	0.24702
0.5984	0.20007
1.1967	0.11042
1.7952	0.04524
2.3936	0.01500
2.9920	0.00429
3.5904	0.00111

Table 3.

	N	$(l; n)$	$E_0\{l, n\}$
a = 0.5	5	$(0; 0, \pm 1, \pm 2)$	-4.8479
	9	$(0; 0, \pm 1, \pm 2)$ $(1; \pm 1, \pm 2)$	-6.0017
a = 1.5	3	$(0; 0, \pm 1)$	-6.0119
	5	$(0; 0, \pm 1)$ $(1; \pm 1)$	-6.2333
a = 3.5	2	$(0; 0)$ $(2; 0)$	-5.9969
	6	$(0; 0)$ $(1; \pm 1)$ $(2; 0, \pm 1)$	-6.1860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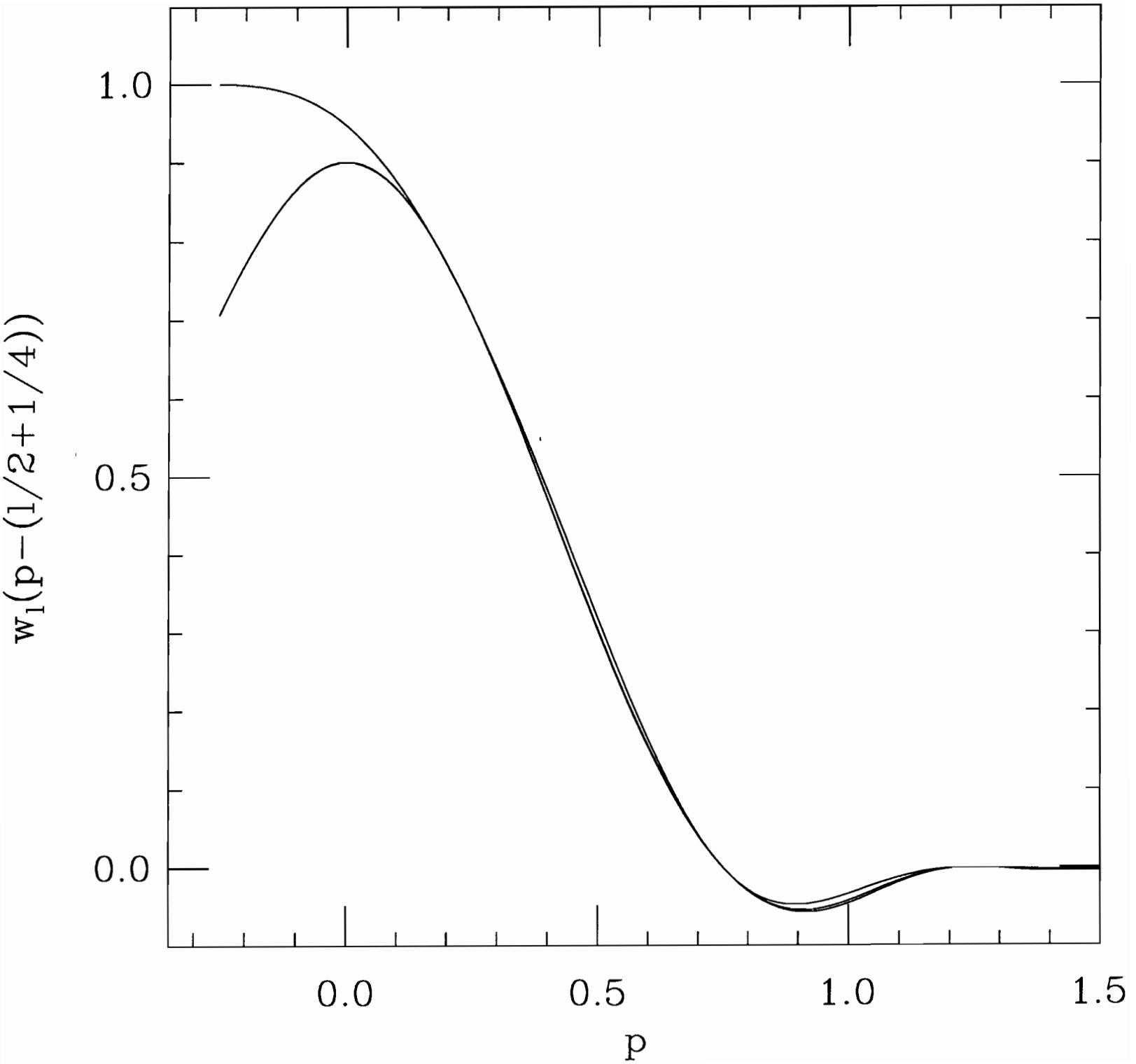
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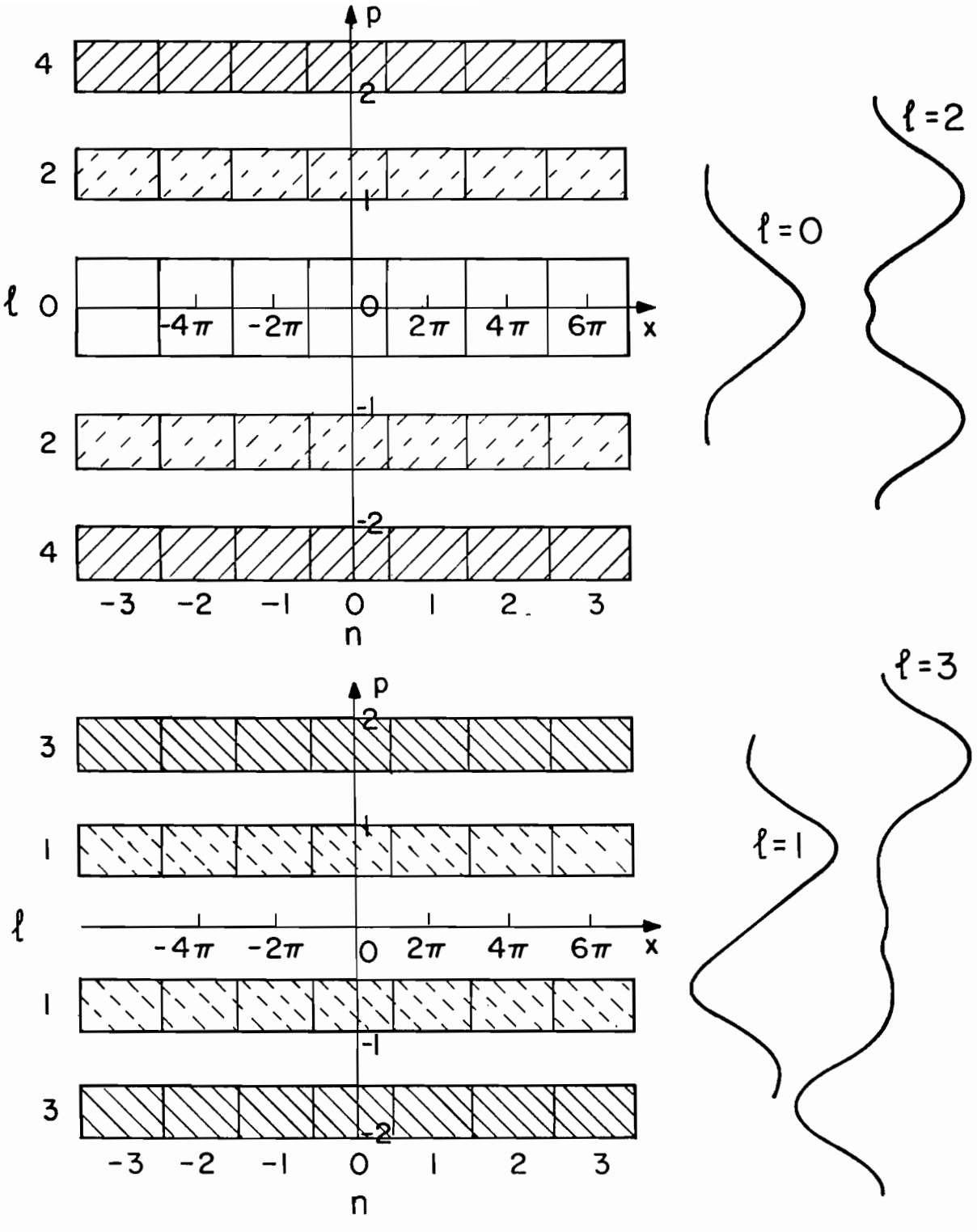
0.5
1.0
1.5
p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n
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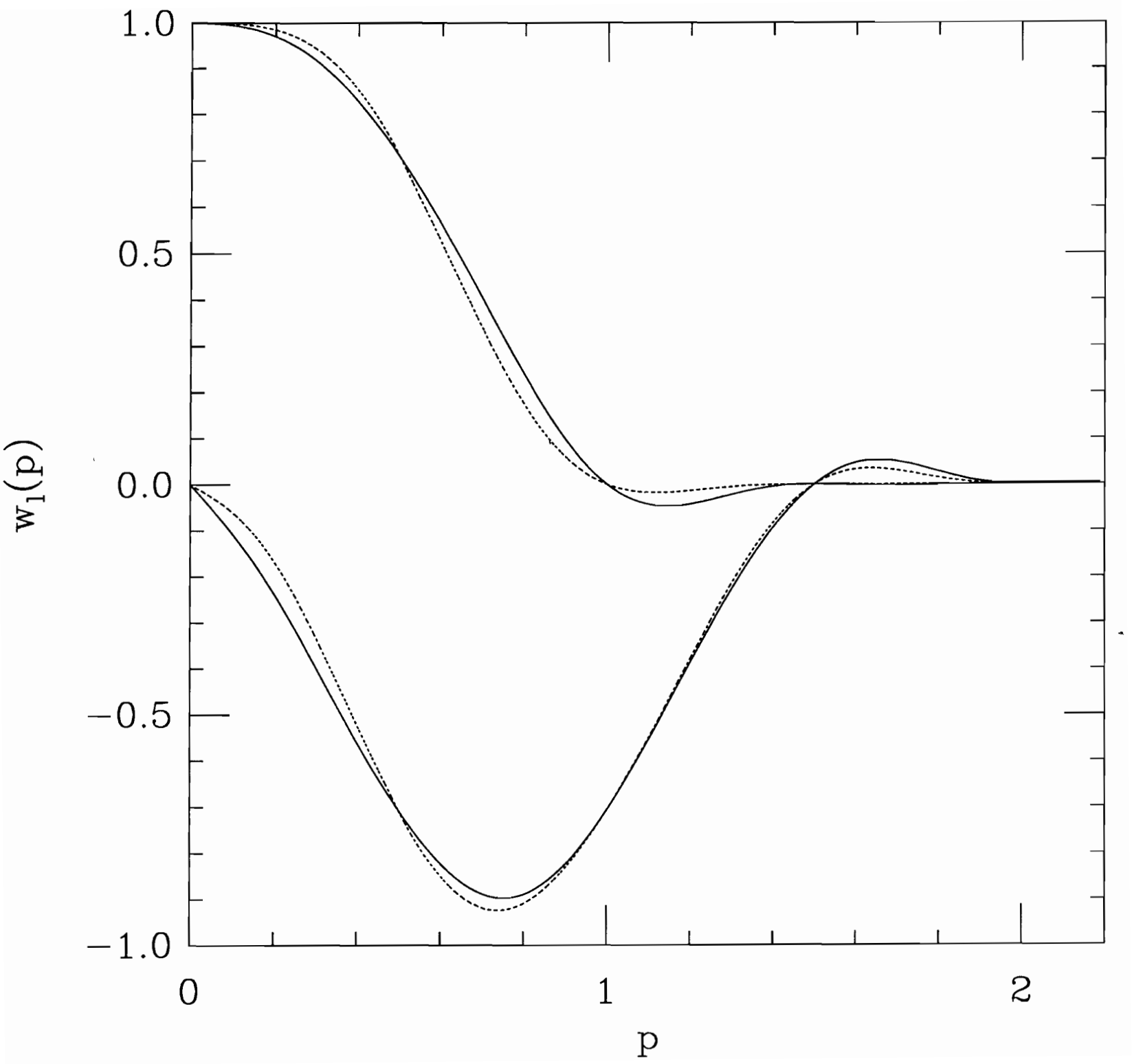
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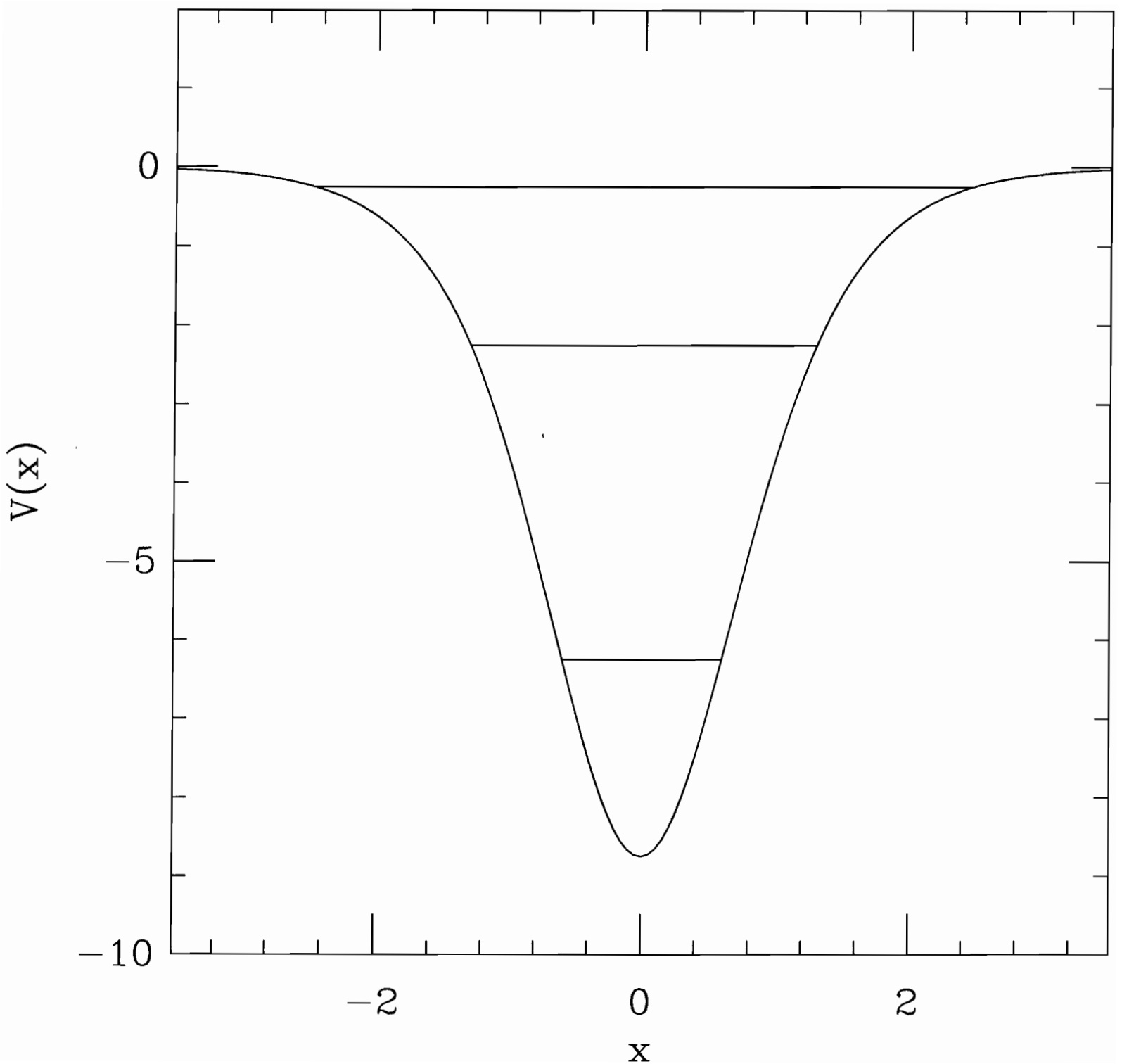
p
$w_1(p)$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p
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